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Abstract:

A reanalysis of polyhedral oligomeric silsesquioxane ions and salts

Brent D. Viers, PRSM, Air Force Research Laboratory, 10 Saturn Blvd., Edwards AFB, CA 93524, Timothy S. Haddad, ERC and Air Force Research Laboratory, Edwards AFB, CA 93524, and Michael T. Bowers, Chemistry, U.C. Santa Barbara, Santa Barbara, CA 93106.

Polyhedral Oligomeric Silsesquioxanes (POSS) are of interest because the hydrolysis and condensation of the silane precursors can be controlled to form incompletely condensed "scaffolds" which can then be functionalized (via condensation) with differing moieties. However, conventional wisdom held that isolation of ionized scaffolds was impossible due to the increased reactivity of the ionic siloxy fragments. However, recent results have shown that certain POSS based salts are indeed stable. This talk will review the progress in formation of ionic species, and the potential of these intermediates for "rational synthesis" of other nanostructures.

FILE

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~~"Structure and Modeling of POSS Monomers"~~ "A Reanalysis of POSS Ions & Salts"

Viers
5416

American Chemical Society Conference   (Statement A)
(New Orleans, LA, 23-27 Mar 2003) (Deadline: 27 Feb 2003 – PAST DUE)

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A reanalysis of polyhedral oligomeric silsesquioxane ions and salts

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†Westmont College

WESTMONT COLLEGE
Santa Barbara
California

A Christian Liberal Arts College

UCSB
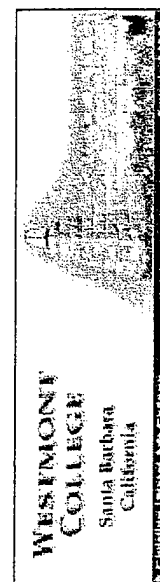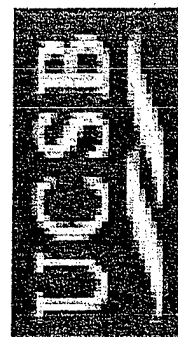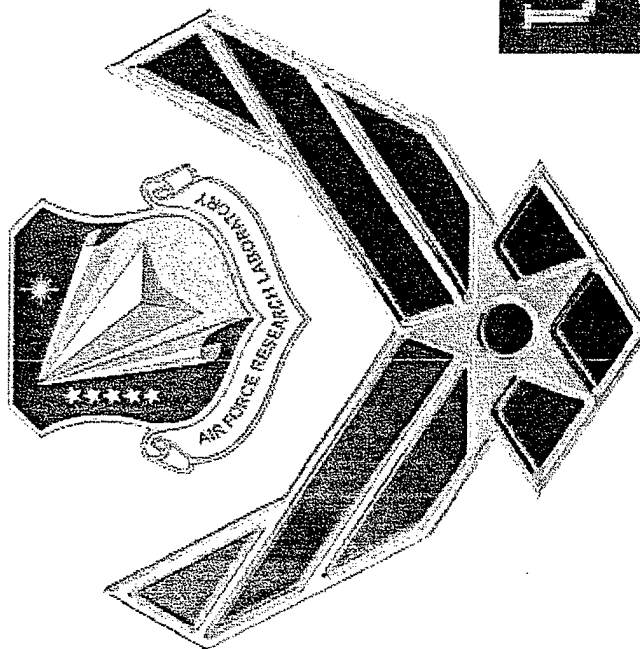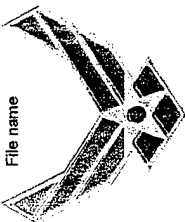
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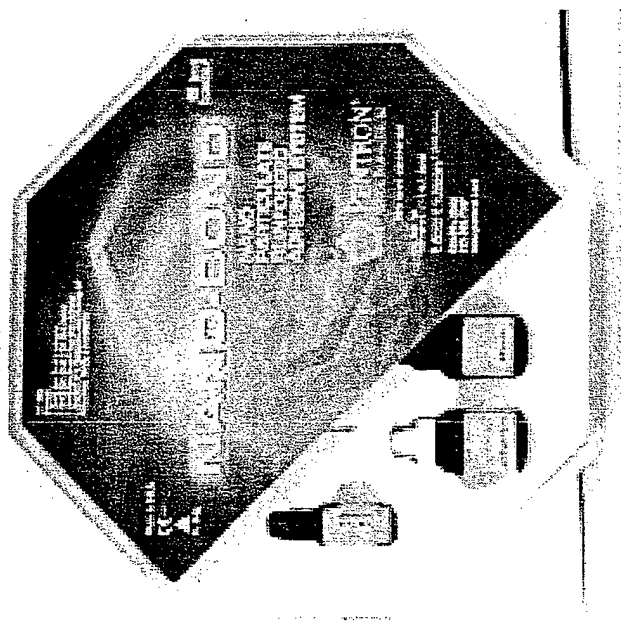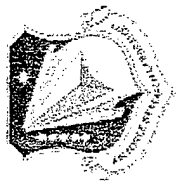
POSS incorporation leads to reduced shrinkage upon cure?
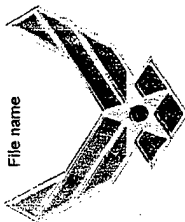
POSSible Structures
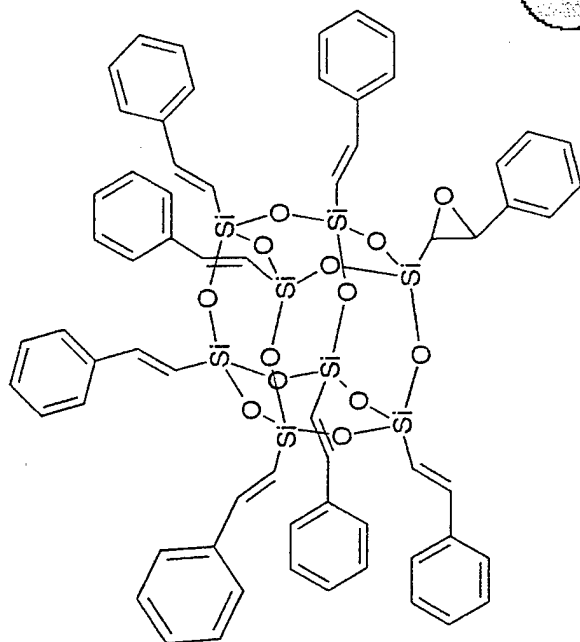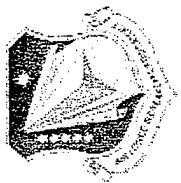
Epoxy POSS Intermediate in Size?
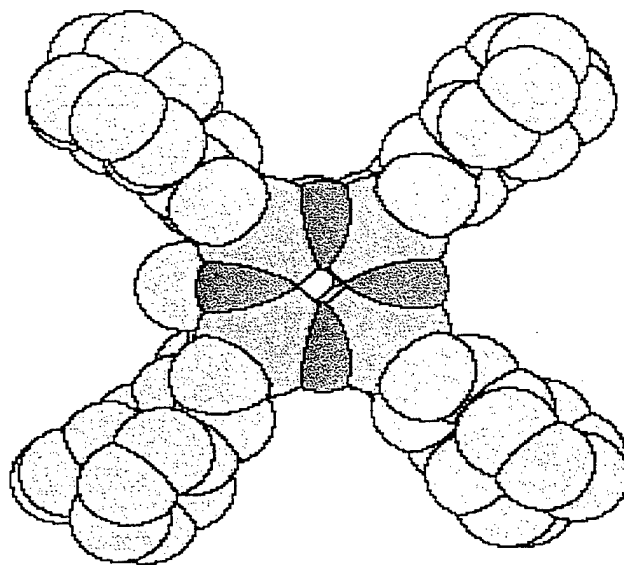
$Na^+Sty_8T_8$

$Na^+PhenEt_8T_8$

File name
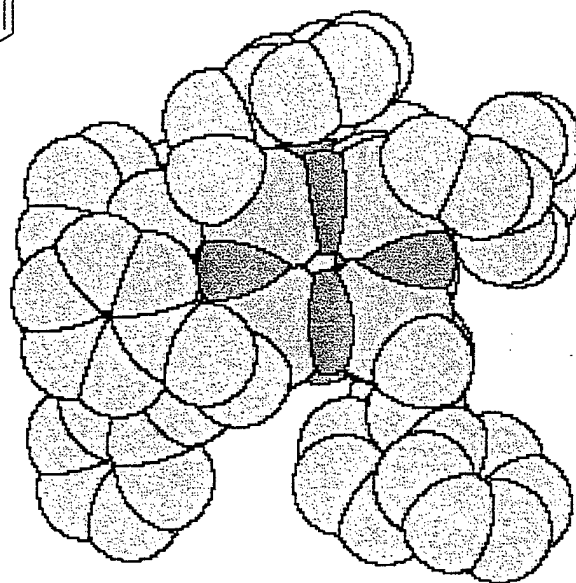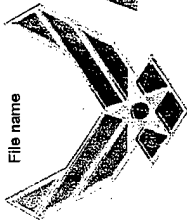
Application Of Ion Mobility Measurements

Ion Mobility

Collision Cross-Sections

Molecular Modeling

3-D Structural Information

Identify Mixture Distributions

Structures of Intermediates

"impurities" in synthesis

How POSS attaches to polymers

Structural differences with different "R" groups

How structure changes with size (POSS oligomers)

4
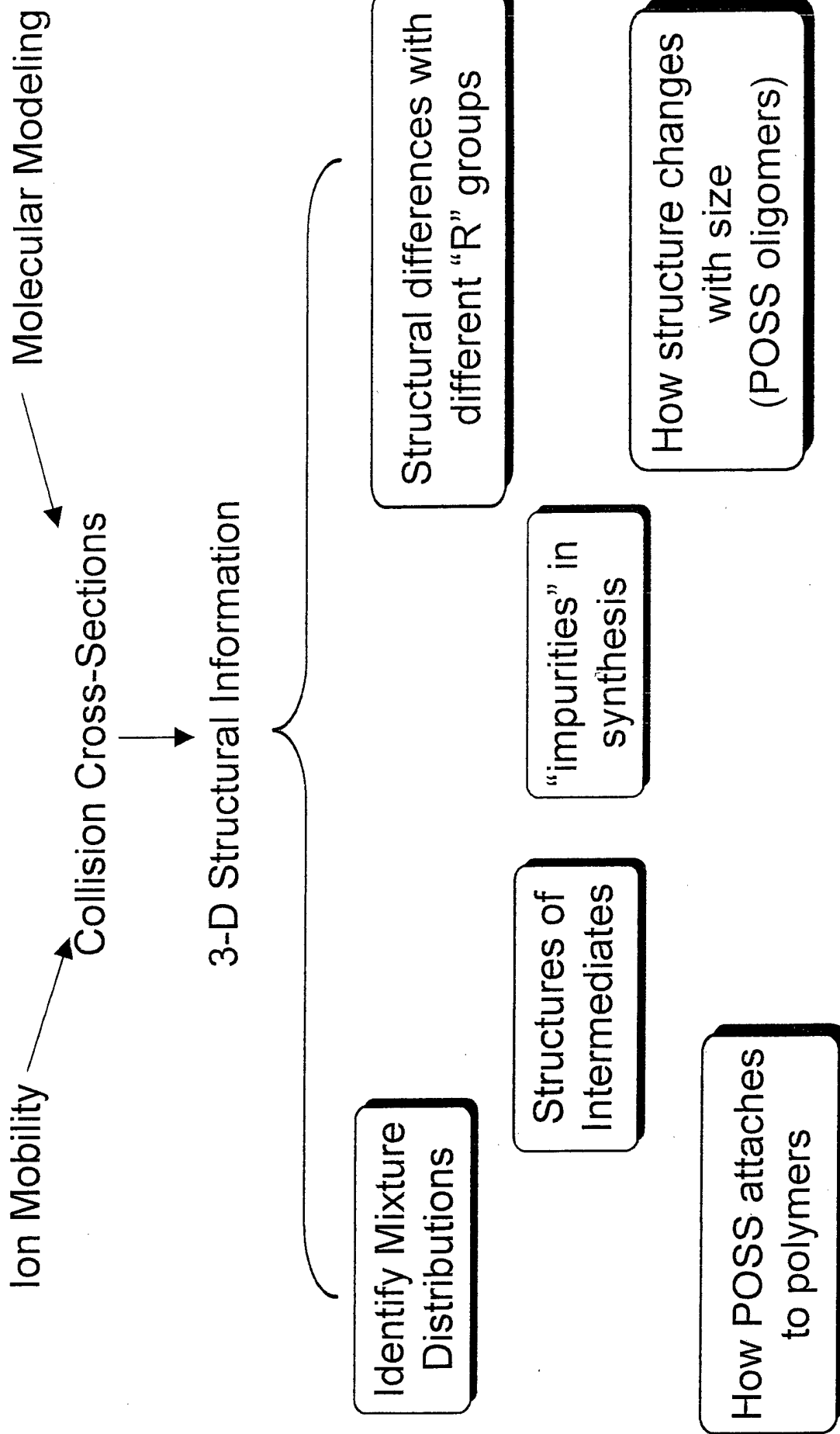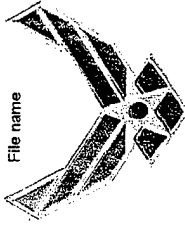
Modifications needed for POSS Modeling
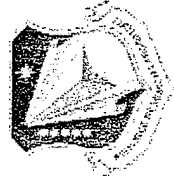
- New parameters for all Si bonds, angles, dihedrals, and torsions (adapted from Si and Si-X parameters obtained from polysiloxane work).

  Ref: H.Sun and D. Rigby, *Spectrochimica Acta A*, 1997, *53*, 1301.

- Atom charges obtained from Gaussian calculations on model systems and x-ray structures; adjusted using AMBER RESP protocol.

- Starting structures built in Hyperchem and imported into AMBER.
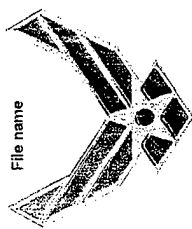
Comparison of Sizes: PhenEt$_8$T$_8$ to Sty$_8$T$_8$

	x-ray	ESI	MALDI	Theory
Na$^+$Sty$_8$T$_8$	341	339	346 [a]	338
Na$^+$PhenEt$_8$T$_8$			267	265 [b]

a) most abundant peak

b) from scatter plot – average value of lowest 7 kcal/mol structures
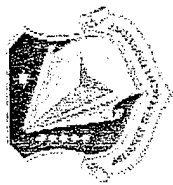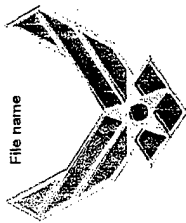
File name

MALDI TOF of Na⁺PhenEt₈T₈

MALDI-TOF Mass Spectrum of Na⁺PhenEt₈T₈

Na⁺PhenEt₈T₈

(Matrix Peaks)

Intensity (arb. units)

m/z

Na⁺PhenEt₈T₈ ATD

arrival time (μS)
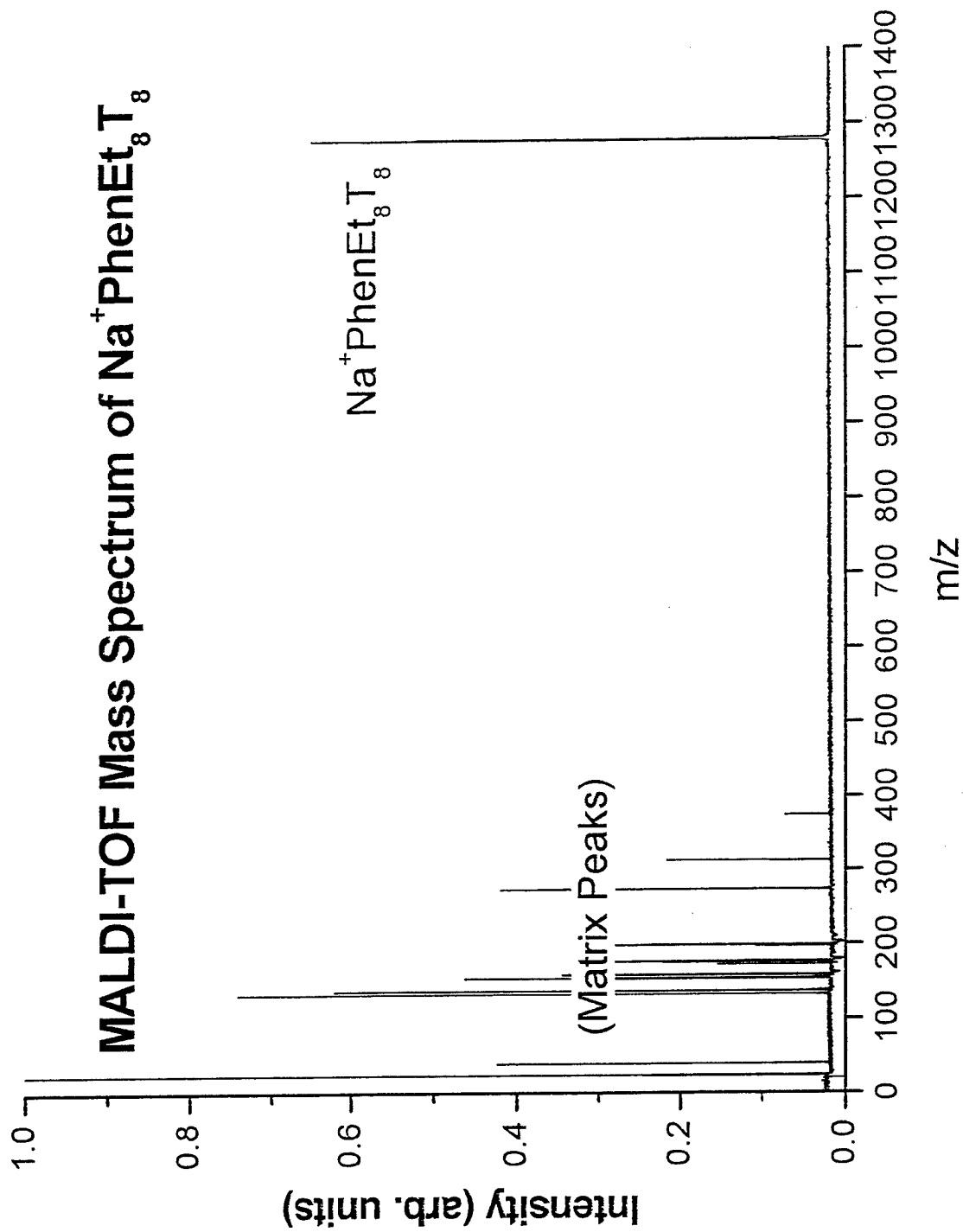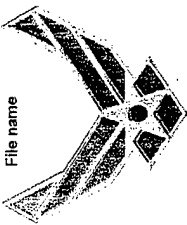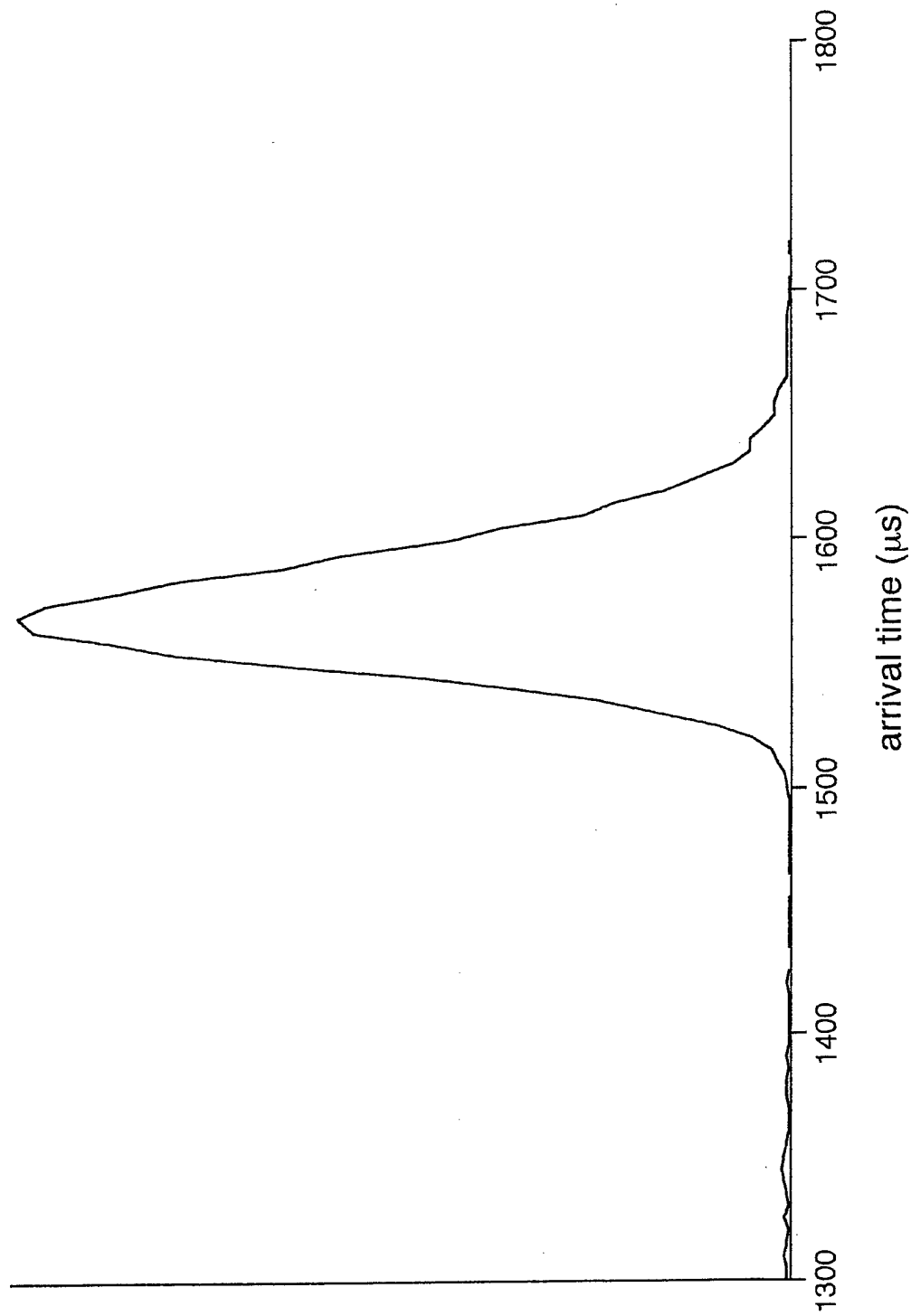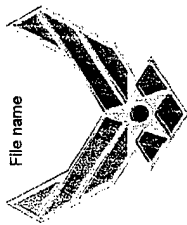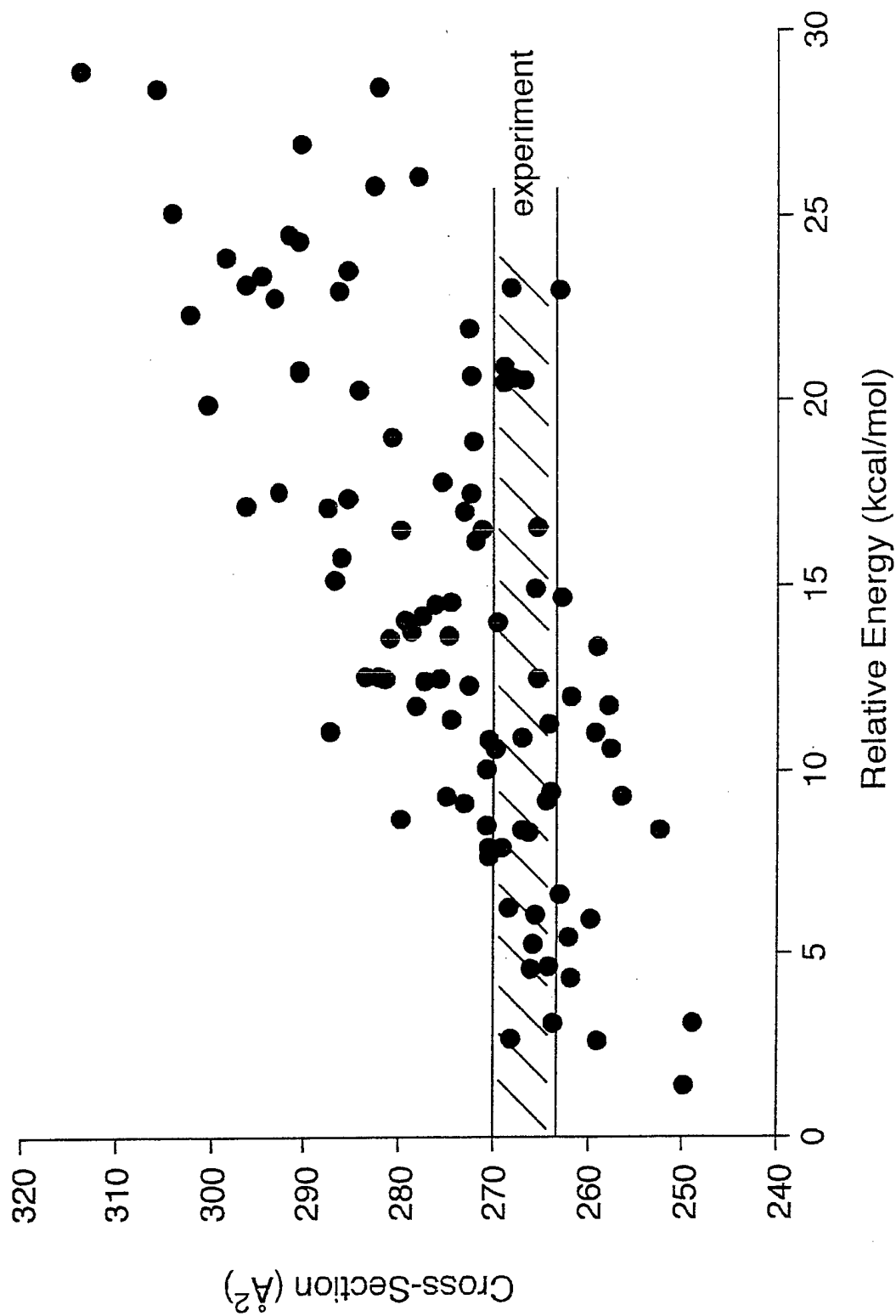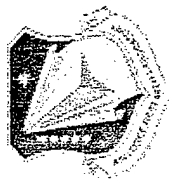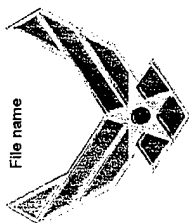
Energetic Calculations

X-ray Structure of Sty$_8$T$_8$

MALDI TOF of Na⁺Sty$_8$T$_8$

relative intensities of peaks follow

statistical pairing of styrenes

(nearest neighbors only)

(2)

(3)

(4)

(5)

(6)

arrival time (µs)

1300   1400   1500   1600   1700   1800
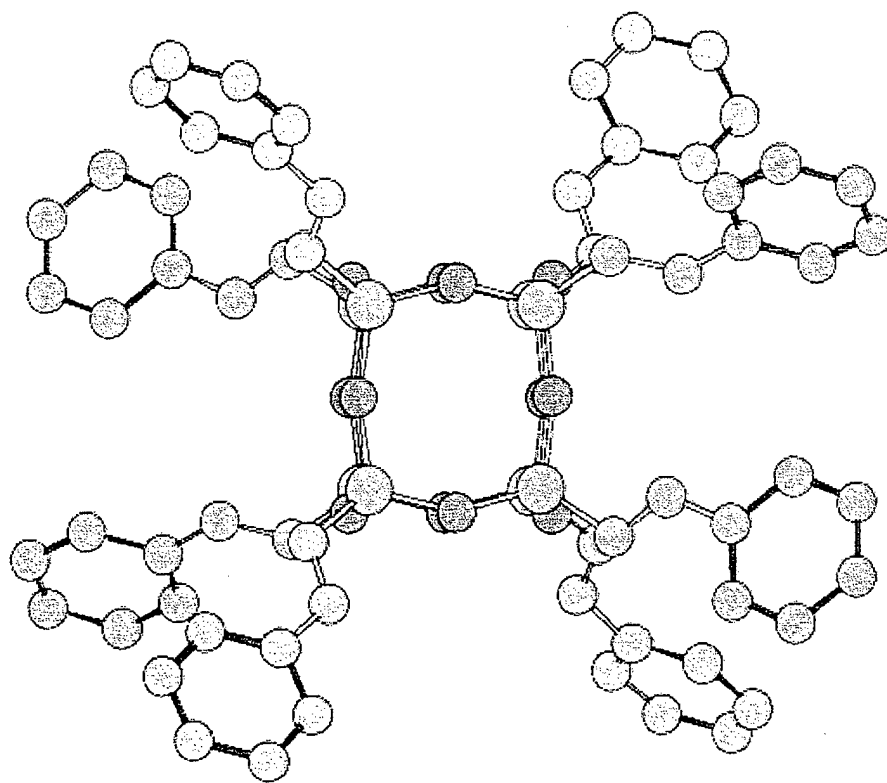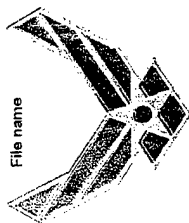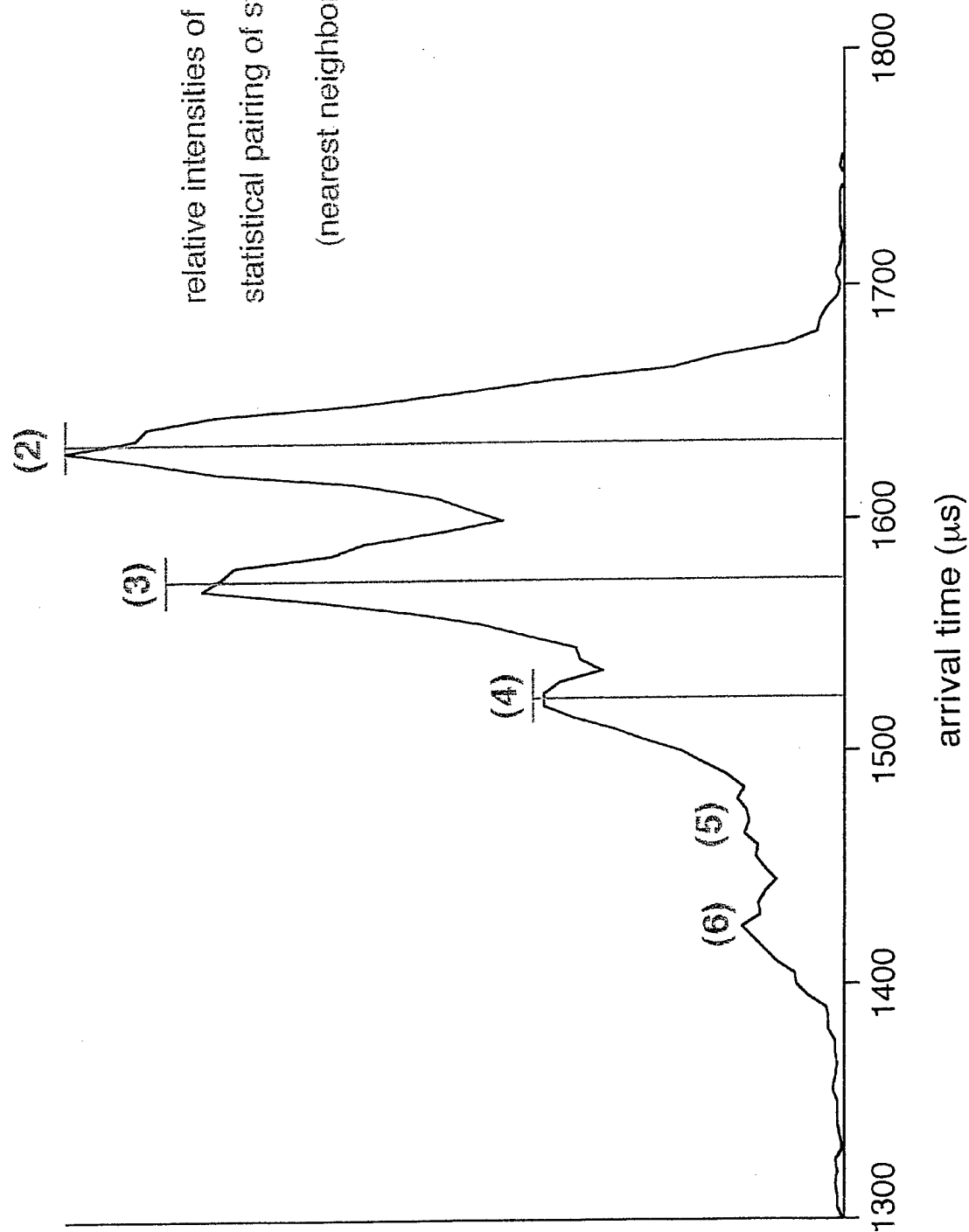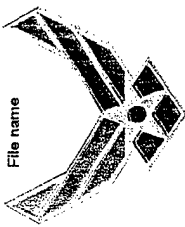
Energetic Calculations
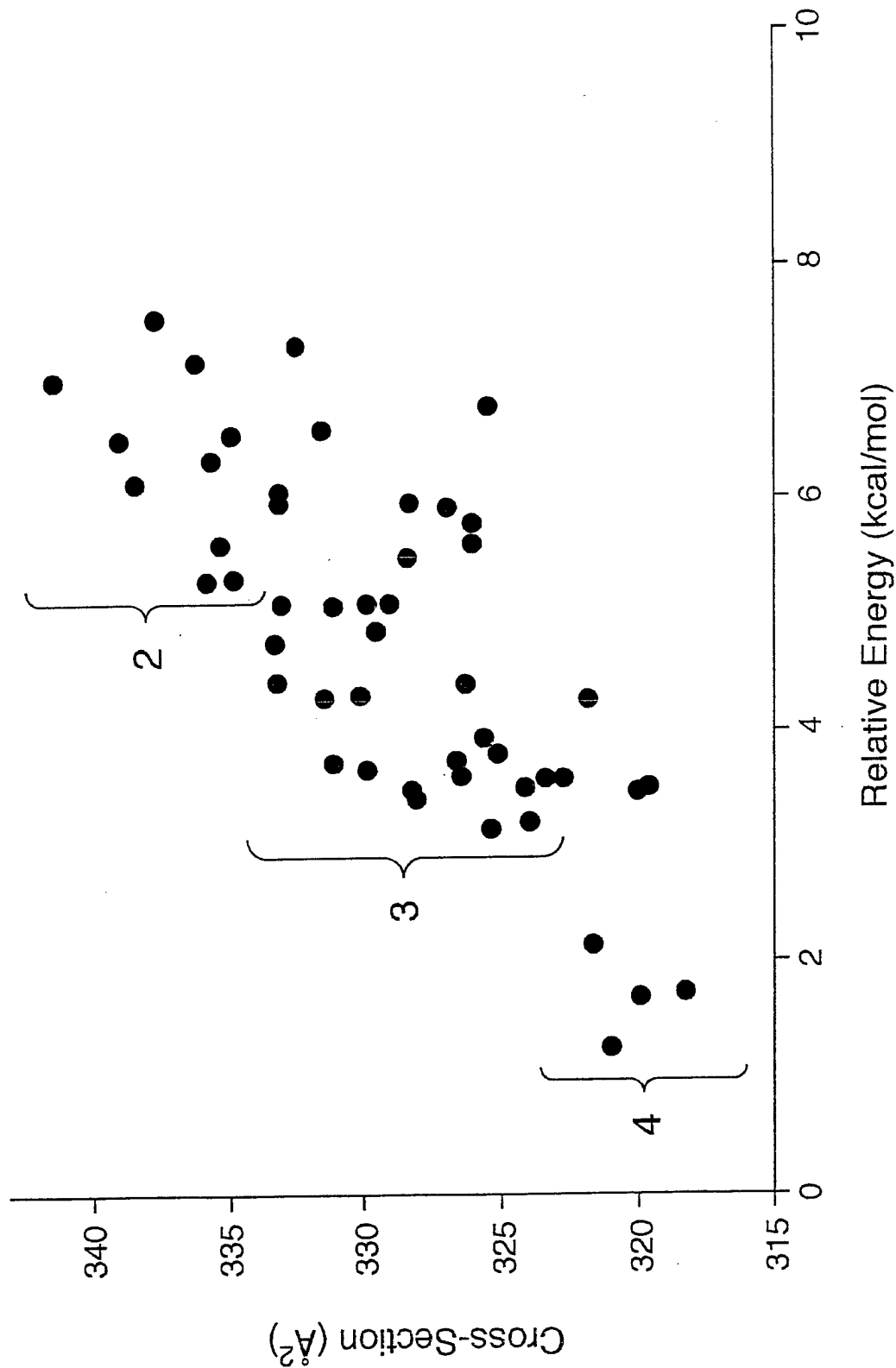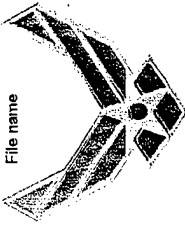
Calculated Na⁺Sty₈T₈ Structures

2 pair

(2)
338 Å²

(3)
328 Å²

3 pair

(4)
320 Å²
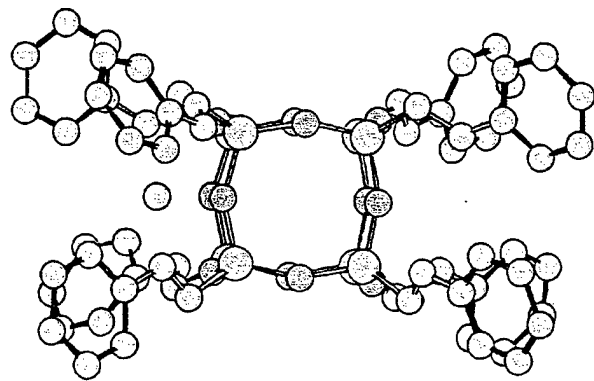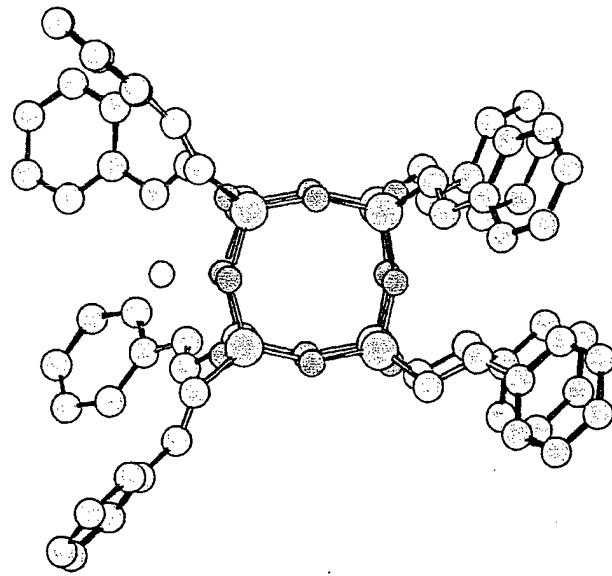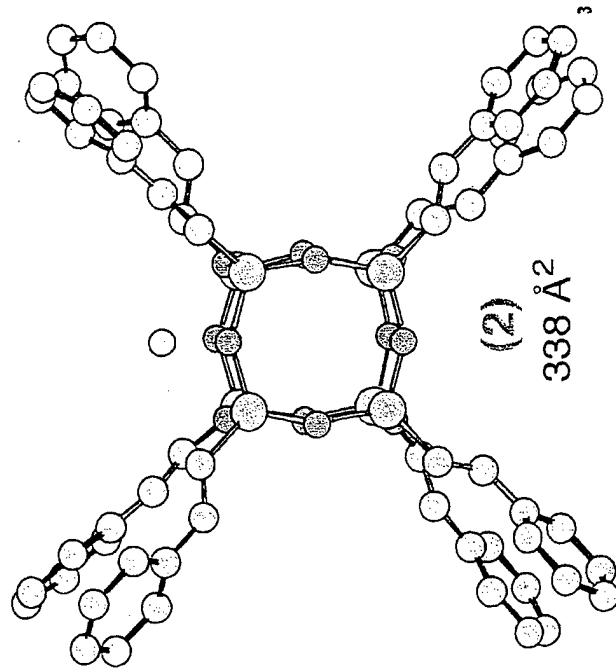
4 pair
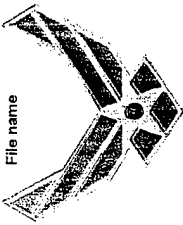
Sty$_8$T$_8$ Cis Defect Structures

paired

paired

Na$^+$

paired

paired

Na$^+$

paired
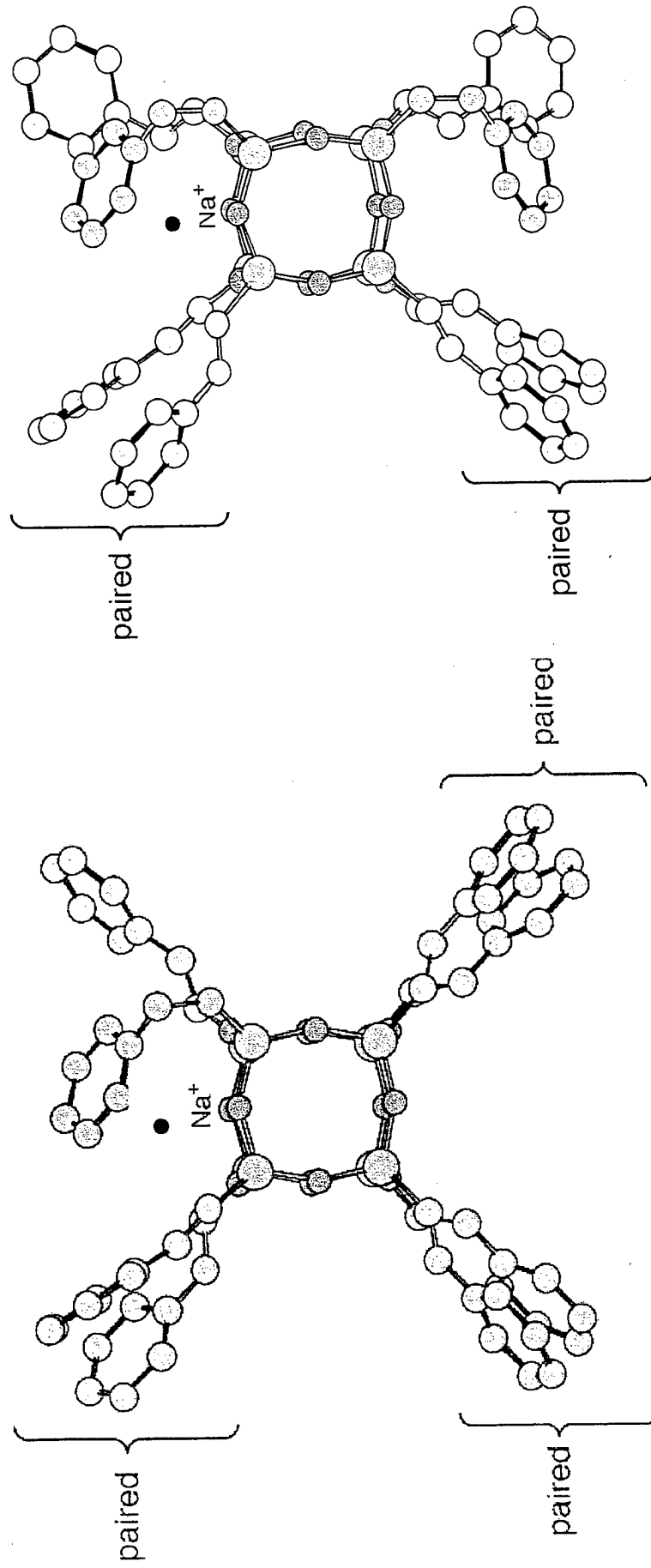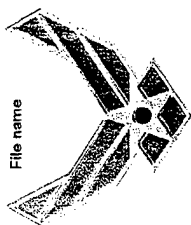
Comparison of Theoretical and Experimental Cross-sections

Theory $\Omega = 338$ Å^2
2 pairs $\Omega_{EXPT} = 340$ Å^2

Theory $\Omega = 328$ Å^2
3 pairs $\Omega_{EXPT} = 330$ Å^2

Theory $\Omega = 320$ Å^2
4 pairs $\Omega_{EXPT} = 324$ Å^2

Theory $\Omega = 295, 307$ Å^2
cis defects $\Omega_{EXPT} = 293, 310$ Å^2

Arrival Time (µs)

1400   1500   1600   1700   1800

File name

15
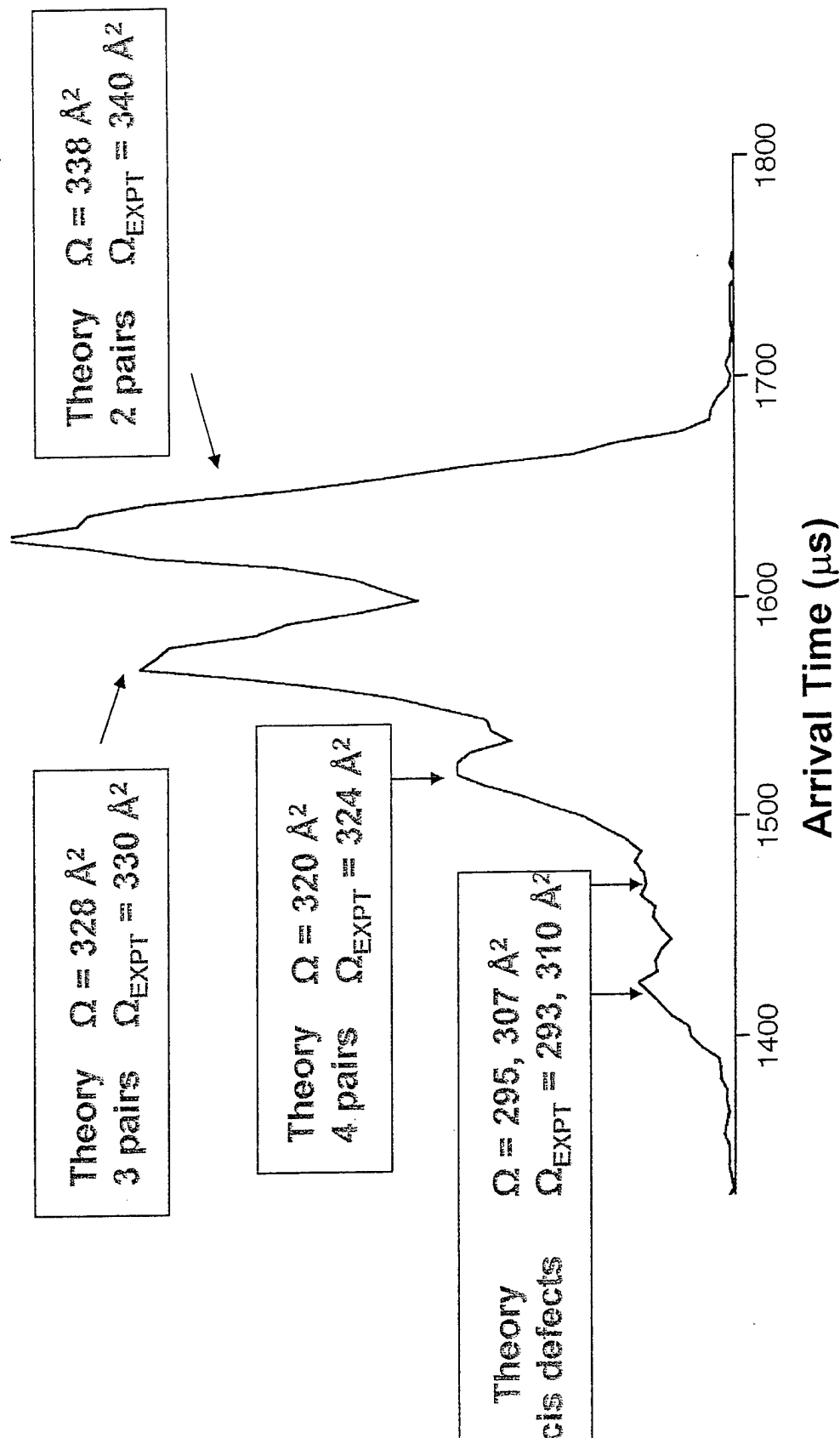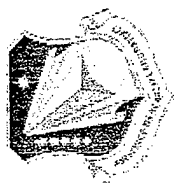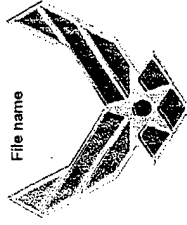
Summary for Sty_8T_8

- Most compact structure (lowest σ) is the most stable

- Least compact structures are most abundant

- Quantitative agreement of experimental and theoretical σ's

- MALDI intensities in semi-quantitative agreement with statistical pairing of phenyl groups

- X-ray structure quantitatively agrees with least compact structure
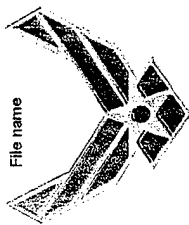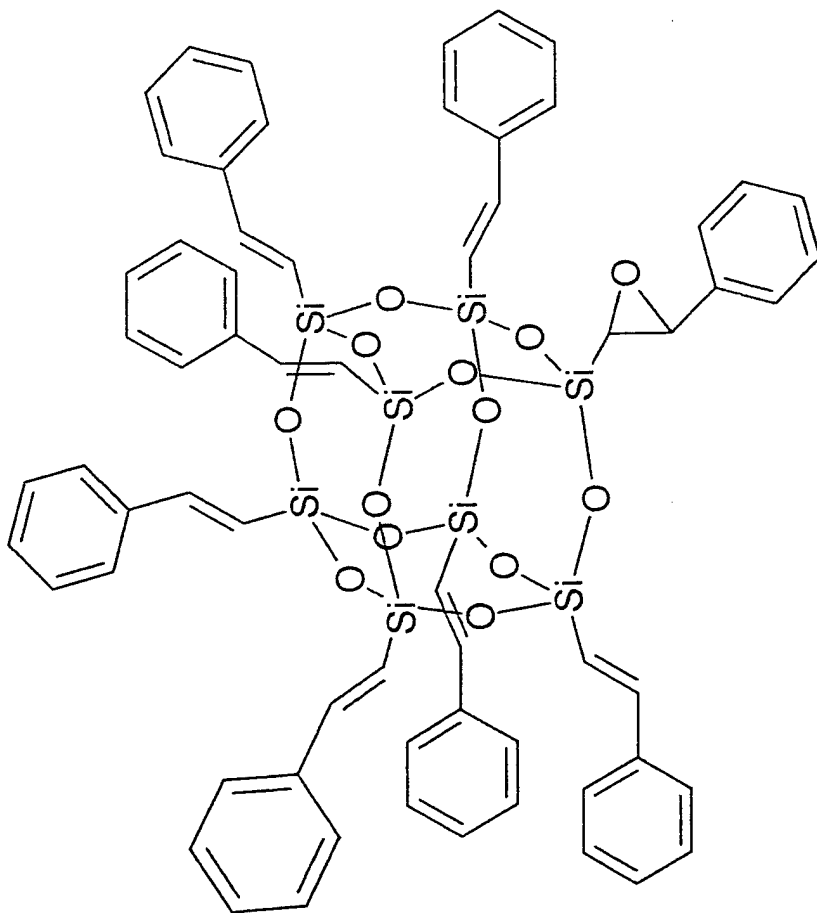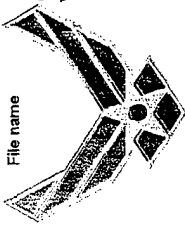
Sty$_7$EpT$_8$

Styrene Epoxy T$_8$ POSS System Mass Spectrum

Ep =

Sty =

Sty$_8$T$_8$

Sty$_7$EpT$_8$

Sty$_5$Ep$_3$T$_8$

Sty$_4$Ep$_4$T$_8$

| 1250 | 1270 | 1290 | 1310 | 1330 | 1350 |

Na⁺Sty₇EpT₈ ATDs

300K

$\sigma = 319 \text{ Å}^2$

$\sigma = 326 \text{ Å}^2$

$\sigma = 323 \text{ Å}^2$

110K
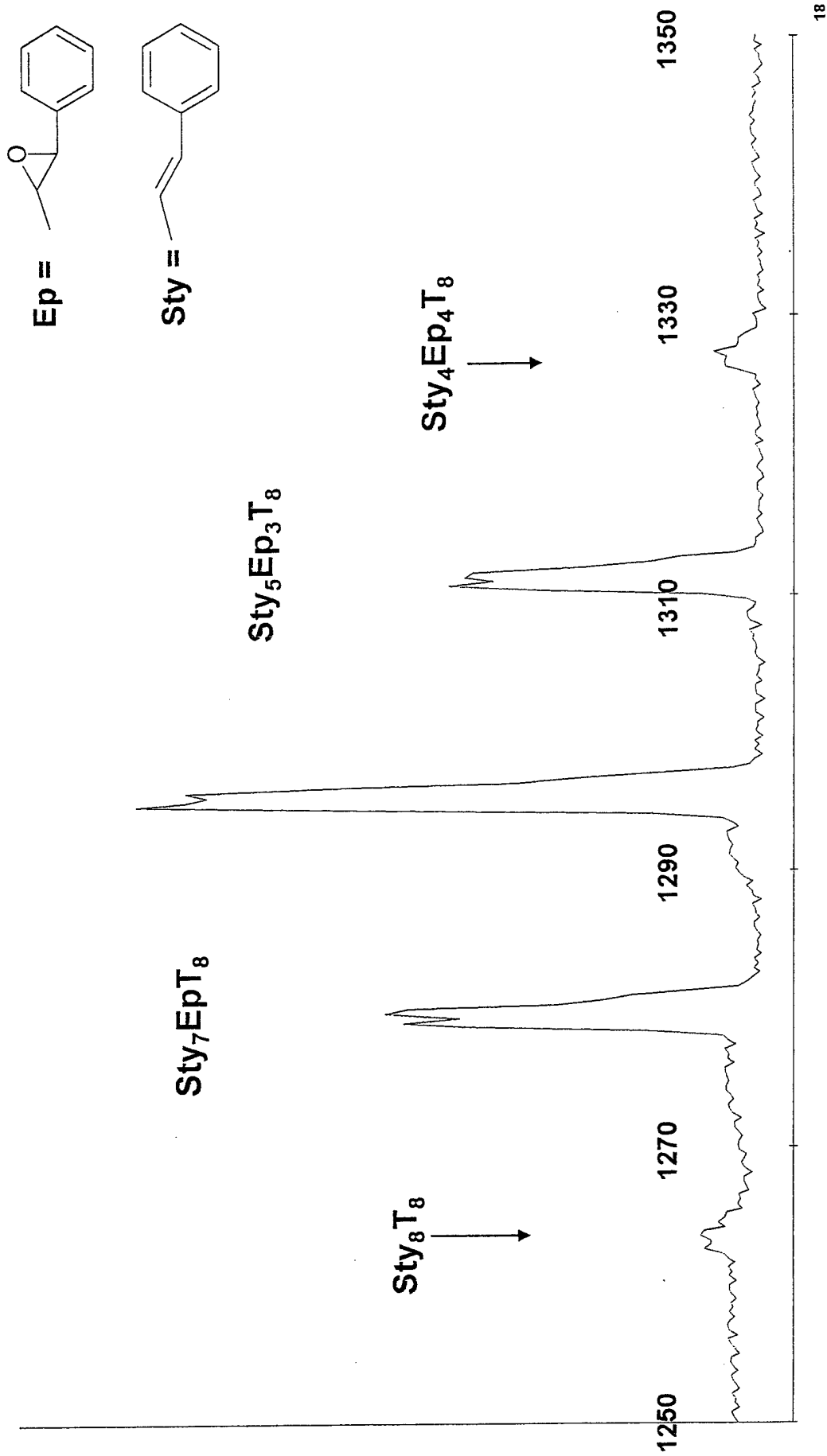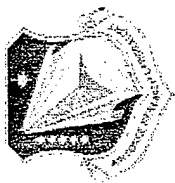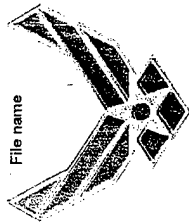
Arrival Time (μs) →
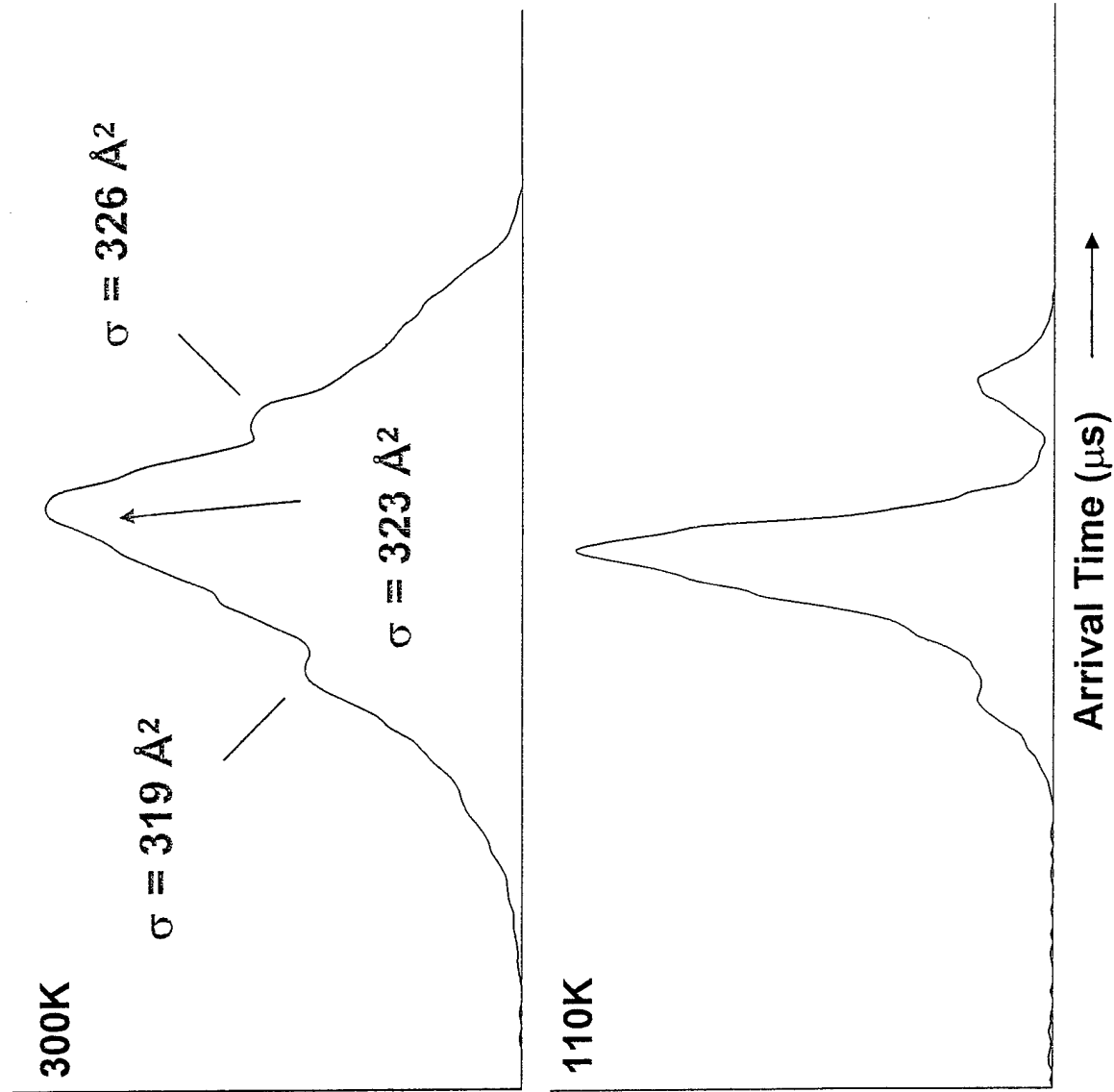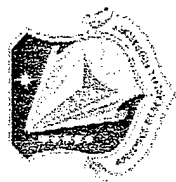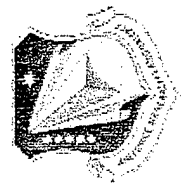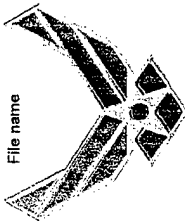
Na$^+$Sty$_7$EpT$_8$ Theoretical Structures
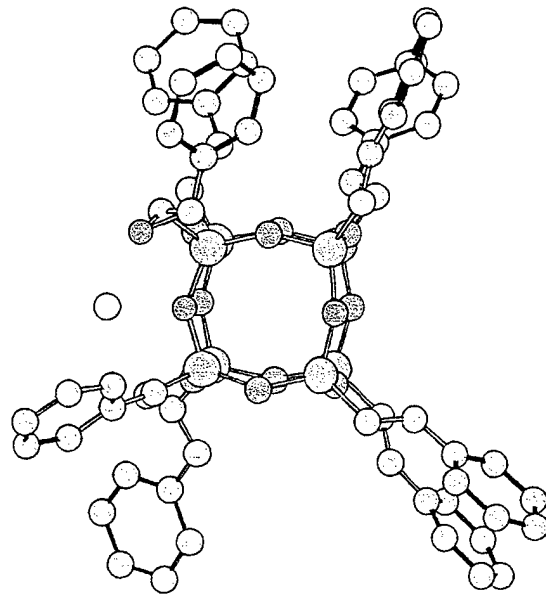
2 Pairs

$\sigma_{Theory} = 320$ Å^2
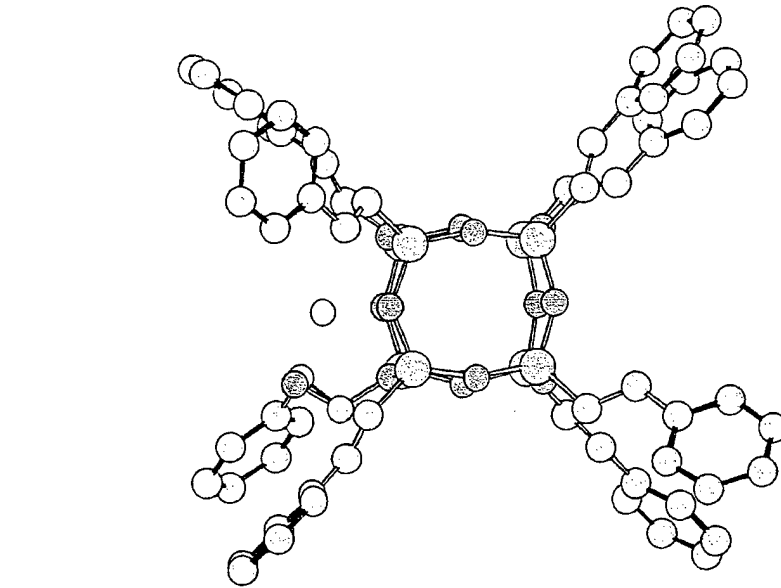
$\sigma_{EXPT} = 319$ Å^2

~13%

No Pairs

$\sigma_{Theory} = 328$ Å^2

$\sigma_{EXPT} = 326$ Å^2

~13%

1 Pair

$\sigma_{Theory} = 324$ Å^2

$\sigma_{EXPT} = 323$ Å^2

~74%

Na+Sty₆Ep₂T₈ ATDs

$\sigma = 324\ \text{Å}^2$

$\sigma = 319\ \text{Å}^2$

$\sigma = 315\ \text{Å}^2$

300K

110K

Arrival Time (µs) ⟶
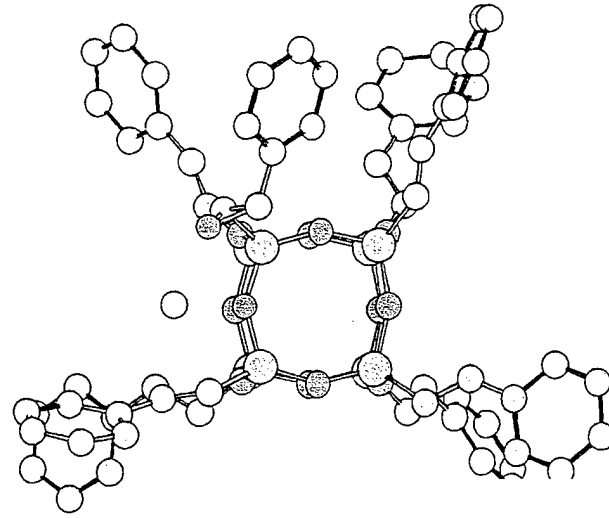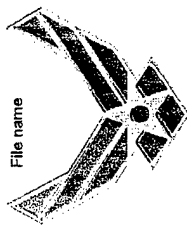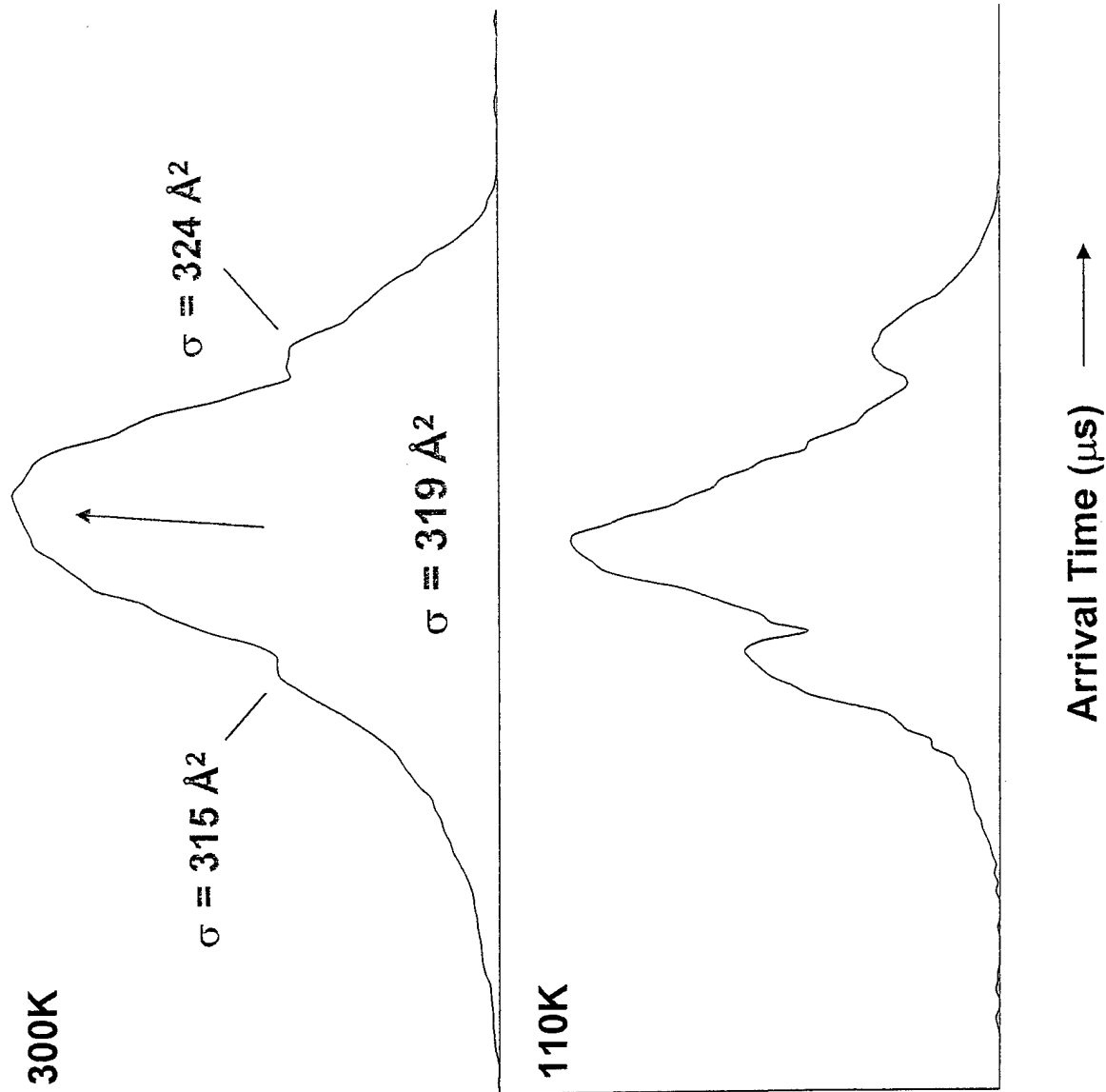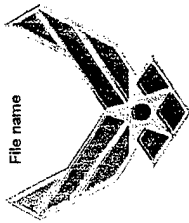
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Na$^+$Sty$_6$Ep$_2$T$_8$ Theoretical Structures
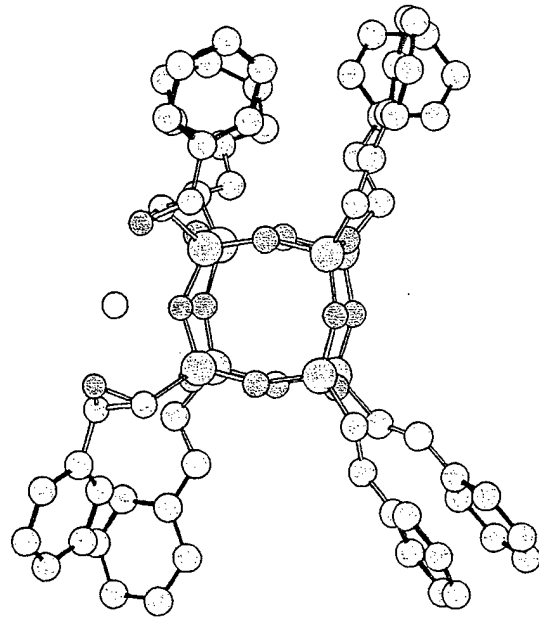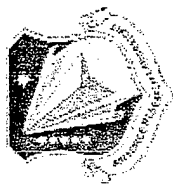
edge
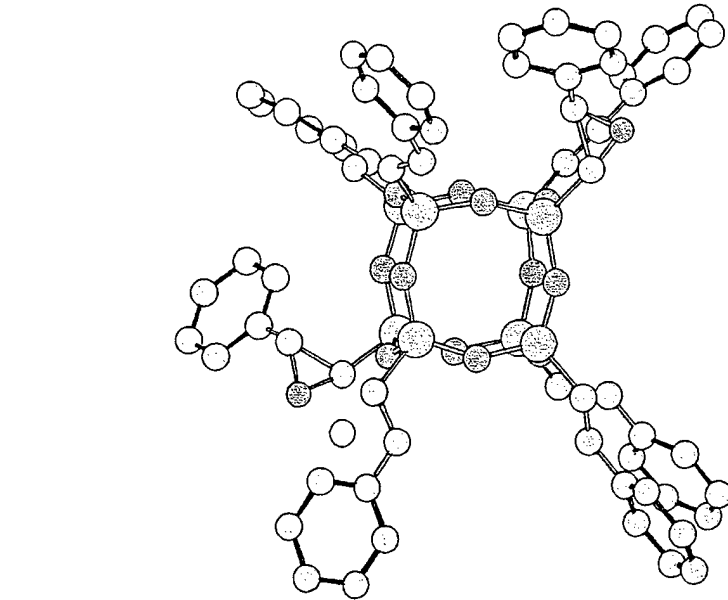
σ_{Theory} = 314 Å^2

σ_{EXPT} = 315 Å^2

~22%

cube diagonal

σ_{Theory} = 322 Å^2

σ_{EXPT} = 324 Å^2

~12%
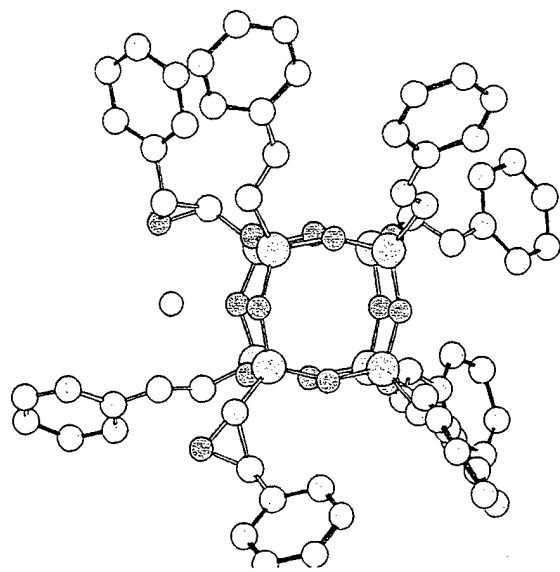
face diagonal

σ_{Theory} = 319 Å^2

σ_{EXPT} = 319 Å^2

~66%

Na⁺Sty₅Ep₃T₈ ATDs

300K

$\sigma = 314$ Å²

$\sigma = 319$ Å²

$\sigma = 327$ Å²

110K

Arrival Time (µs)
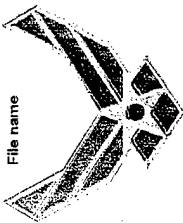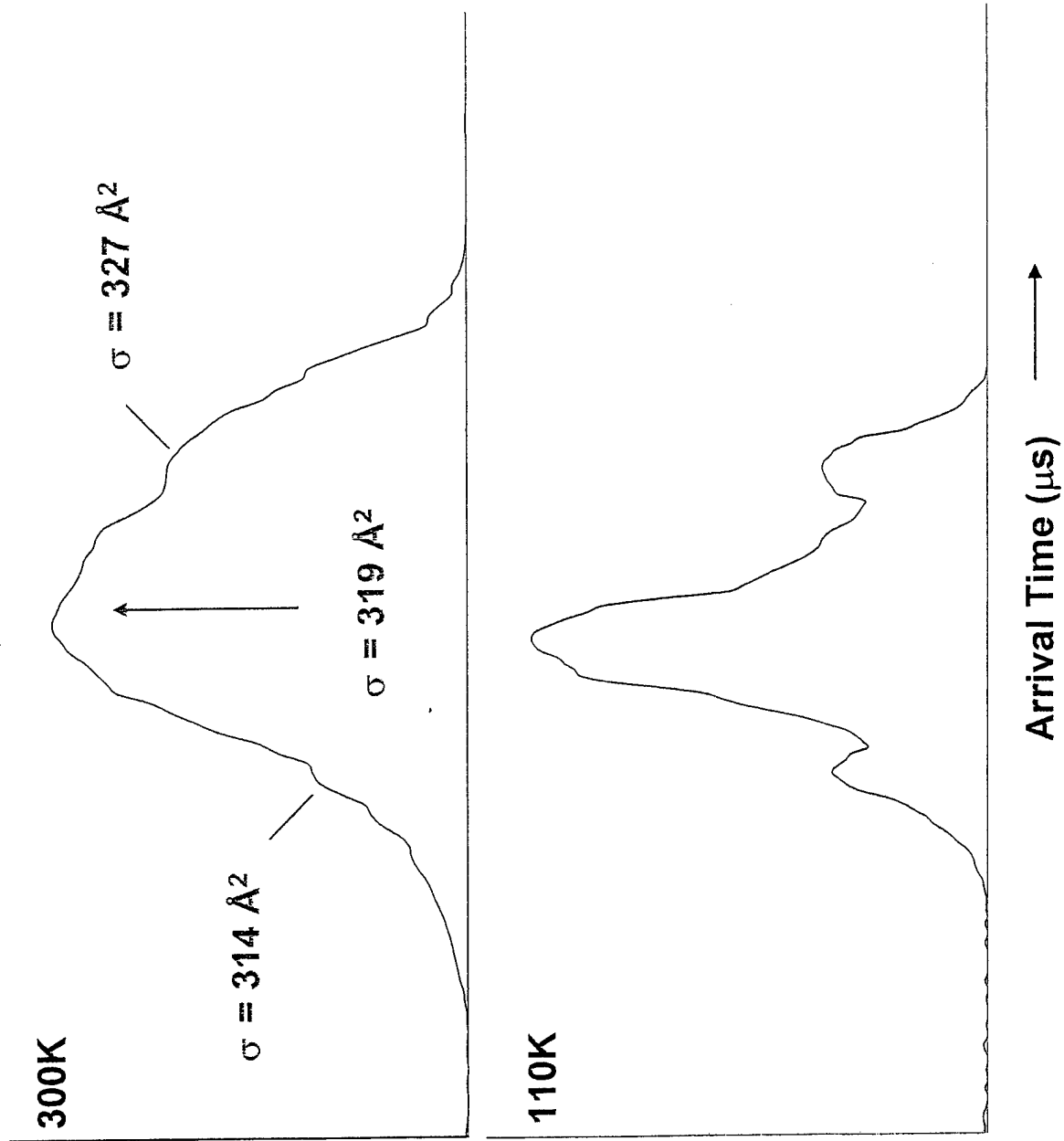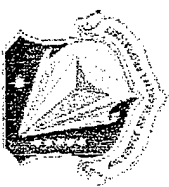
Na⁺Sty₅Ep₃T₈ Theoretical Structures

3 on face diagonals

$\sigma_{Theory} = 326$ Å²

$\sigma_{EXPT} = 327$ Å²

~17%
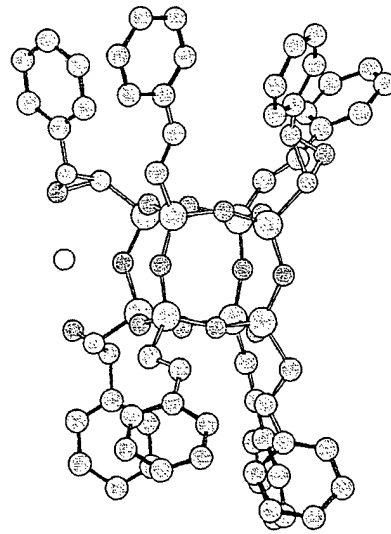
2 adjacent and 1 on the opposite edge:

$\sigma_{Theory} = 319$ Å²

$\sigma_{EXPT} = 319$ Å²

~66%

3 epoxides adjacent on face

$\sigma_{Theory} = 314$ Å²
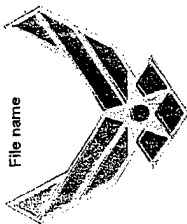
$\sigma_{EXPT} = 314$ Å²

~17%
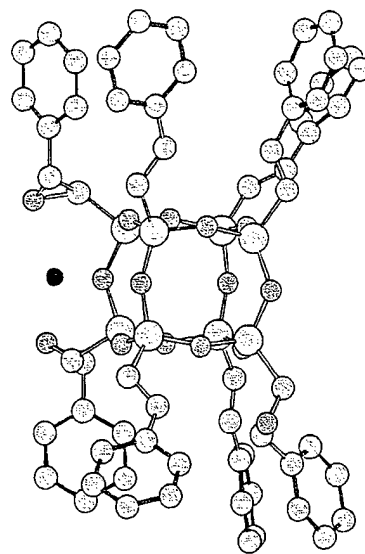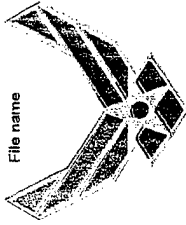
Summary for Styrene Epoxy T_8 POSS System

- For a given x, y the distribution of the geometric isomers can be obtained from ion mobility studies

- Can determine x, y distributions of $Sty_xEp_yT_8$ from mass spectrum

- Size of Epoxy intermediate between Sty_8T_8 and $PhenEt_8T_8$

- *Future Work*: Model Hardening reactions with Monofunctional Amine Reagents

Acknowledgments
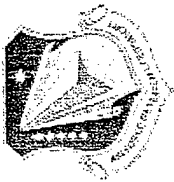
Erin Baker

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File name